From: HOPE Bruce

To: <u>Eric Blischke/R10/USEPA/US@EPA</u>

Subject: RE: SRP Research Brief 176: A New Analytical Method to Support Studies of Mercury Bioavailability in Aquatic

Ecosystems

Date: 08/13/2009 03:04 PM

Thanks!

From: Blischke.Eric@epamail.epa.gov [mailto:Blischke.Eric@epamail.epa.gov]

Sent: Thursday, August 13, 2009 9:19 AM

To: HOPE Bruce

Subject: Fw: SRP Research Brief 176: A New Analytical Method to Support Studies of Mercury

Bioavailability in Aquatic Ecosystems

Bruce, you may be in the loop on this but just in case.

Eric

----- Forwarded by Eric Blischke/R10/USEPA/US on 08/13/2009 09:16 AM -----

BONNIE ELEDER/R5/USEPA/US

To

08/13/2009 06:43 AM

Subject Fw: SRP Research Brief 176: A New Analytical Method to Support Studies of Mercury Bioavailability in Aquatic Ecosystems

FYI....Development of a new analytical method to support studies of mercury bioavailability in aquatic ecosystems:

Researchers are conducting studies to identify the mechanisms underlying movement of Hg and methyl mercury (MeHg) through reservoir and estuarine foods webs into fish and shellfish and ultimately, humans. A method to quantify total metals and of metal speciation in very low biomass samples such as zooplankton, polychaetes, amphipods, and snails is needed in support of these studies. Methods have been developed to address this need.

"This work provides a new avenue for sequential determination of MeHg and total Zn, As, Se, Cd, Hg, and Pb in biological samples with dry sample weight less than 50 mg. This method also requires less sample preparation time than previous methods.

This ability to analyze small samples is critical to ecological research like that conducted by Dr. Chen. For example, metal uptake in aquatic organisms varies with size and age, particularly when the diet of an organism changes throughout its lifecycle. This new method will allow researchers to analyze individual whole organisms or extremely small samples of organisms at the base of the food web. This will contribute to the understanding of how metals move into aquatic food webs. In addition, differences between bioaccumulation of different heavy metals have been observed (e.g., Hg vs. As and Pb). Finally, determination of both MeHg and total heavy metal concentration in individual organisms will allow researchers to identify relationships between the uptake of different metals by aquatic organisms, their food sources, and their positions in the food web."

Please see below for further information...

---- Forwarded by BONNIE ELEDER/R5/USEPA/US on 08/13/2009 07:47 AM -----

Maureen Avakian <avakian@niehs.nih.gov> Sent by: sbrp-brief-bounces@list.niehs.nih.gov

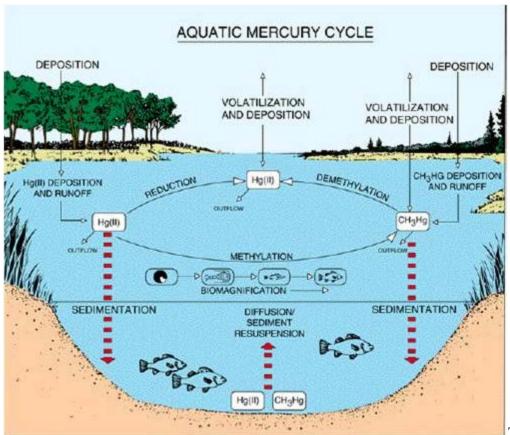
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Research Brief 176: A New Analytical Method to Support Studies of Mercury Bioavailability/Bioaccumulation in Aquatic Ecosystems

Background: Mercury (Hg) enters the environment from natural and anthropogenic sources and readily moves into the biosphere, eventually making its way into all water bodies. An interdisciplinary team of ecologists, biogeochemists, trace metal chemists and modelers, directed by Dr. Celia Chen at the Dartmouth College SRP, is investigating the natural processes regulating the fate of Hg and other metals across several orders of biological complexity.



The ultimate

goal is to develop a mechanistic understanding of the vital links between human and environmental health. They are using extensive field surveys, mechanistic experiments, and detailed analytical and statistical models to discover the mechanisms underlying movement of Hg and methyl mercury (MeHg) through reservoir and estuarine foods webs into fish and shellfish and ultimately, humans.

These studies require quantification of total metals and of metal speciation in very low biomass samples such as zooplankton, polychaetes, amphipods, and snails. In a collaboration with Dartmouth Trace Element Analysis Core Director Dr. Brian Jackson and postdoctoral researcher Dr. Vivien Taylor, the team has developed methods to address these analytical challenges.

Advances: Determination of total metal concentration and Hg species in a sample are usually conducted independently on individual sub-samples. For low biomass samples it is not possible to sub-divide the sample for these two analyses. Drs. Taylor and Jackson built upon an acid leach method to develop a method capable of measuring MeHg as well as total metals (zinc [Zn], arsenic [As], selenium [Se], cadmium [Cd], Hg, and lead [Pb]) in low-mass samples by inductively coupled plasma mass spectrometry (ICP-MS).

Because Hg biomagnifies in aquatic ecosystems, mostly as MeHg, determination of Hg species is crucial to toxicity and uptake studies.

Analysts first spike the sample with enriched stable isotopes of MeHg and inorganic Hg. The Hg species are extracted by a weak acid leach and

are quantified by isotope dilution purge and trap gas chromatography coupled to ICP-MS. Because of the extremely high sensitivity of this approach it only uses 1% of the total acid leach extract. The remainder is then acidified with an equal volume of concentrated HNO₃ and microwave digested under high temperature and pressure. This digested solution is then analysed for total metal concentration by collision cell ICP-MS.

The researchers verified the method using five certified reference materials (lobster hepatopancreas, dogfish muscle, oyster tissue, mussel tissue, and plankton). Measured values for MeHg ranged from 93% to 114% of the certified value, suggesting that the extraction method is robust for a wide array of samples. Total metal concentrations were also in good agreement with certified values, with average recoveries from 97.1% to 103.5% of the reference values. The levels of accuracy and precision are well within the EPA-recommended quality control criteria.

The researchers then compared the sum of the Hg species determined from the speciation step of the analysis with total Hg determined from the total metals analysis on 285 invertebrate and fish samples. The researchers found excellent agreement between the sum of mercury species and total mercury, indicating that the isotope dilution approach for Hg species quantification is effective for inorganic Hg in addition to MeHg.

Significance: This work provides a new avenue for sequential determination of MeHg and total Zn, As, Se, Cd, Hg, and Pb in biological samples with dry sample weight less than 50 mg. This method also requires less sample preparation time than previous methods.

This ability to analyze small samples is critical to ecological research like that conducted by Dr. Chen. For example, metal uptake in aquatic organisms varies with size and age, particularly when the diet of an organism changes throughout its lifecycle. This new method will allow researchers to analyze individual whole organisms or extremely small samples of organisms at the base of the food web. This will contribute to the understanding of how metals move into aquatic food webs. In addition, differences between bioaccumulation of different heavy metals have been observed (e.g., Hg vs. As and Pb). Finally, determination of both MeHg and total heavy metal concentration in individual organisms will allow researchers to identify relationships between the uptake of different metals by aquatic organisms, their food sources, and their positions in the food web.

For more information, contact:

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To learn more about this project, please refer to the following sources:

Taylor, V.F., B.P. Jackson, and C.Y. Chen. 2008. Mercury speciation and total trace element determination of low-biomass biological samples. *Anal. Bioanal. Chem.* **392**:1283-1290. Available online: DOI:10.1007/s00216-008-2403-3

Jackson, B., Taylor, V., Baker, R.A., Miller, E. 2009. Low-level mercury speciation in freshwaters by isotope dilution GC-ICP-MS. *Envr. Sci. Toxicol*.43(7):2463-9. Available online: DOI: 10.1021/es802656p

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